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Characteristics of Pyrolysis Products of Bori Lignite Briquette

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Abstract

In this paper pyrolysis experiment of the binderless hot-briquetted lignite were studied and the production characteristics of semi-coke、tar and gas were analyzed. The results indicated: Along with the increase of pyrolysis temperature, the H/C of the semi-coke and the O element content reduced obviously, but both falling strength and compressive strength of the semi-coke were increased. When the pyrolysis temperature reached 650˚C, the O element has completely released, and the falling and compressive strength reached 60.88% and 157.24N when the pyrolysis temperature reaches 700℃.The semi-coke SEM changed from honeycomb-like structure to softening surface and collapsed cracks with the pyrolysis temperature rising from 400˚C to 800˚C. The volatile has released entirely above 800˚C, while the tar yield reached the highest of 3.39% in 550℃. Furthermore, the volume of CH_4, C_2~C_4 and H_2 reached maximum at 750˚C, 600˚C and 800˚C, with their values being 0.80L/min, 0.12 L/min and 2.79 L/min respectively.

Key words: pyrolysis characteristics; the binderless hot-briquetted lignite; semi-coke; tar; gas

1. Introduction

Lignite is a low rank coal, which's metamorphism is between peat and bituminous coal. Lignite contains highly moisture and oxygen, but has a low fixed carbon and calorific value, and it's easy to weathering and spontaneous combustion in the air[1]. So it's difficult to long-term store the lignite and not worth to transport long-distance. One of the main methods to upgrading the lignite and to improve its use of value, is drying and shaping[2]. A 100 t/a production of hot press binderless lignite briquette line has been established in Baori; Yunnan and Xinjiang provinces are also being planned to establish the

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project of Binderless hot-briquette preparation from lignite. Although lignite decreased in moisture, increased in heating value and became a high-quality fuel by hot press upgrading, it is easy to crack and re-adsorb water and fail to store or transport. Therefore, The use of deep processing of lignite-briquette need further study.

Through pyrolysis, the lignite briquette is transformed to the briquette semi-coke which can be used as carbon reducer, high-quality gasification material and fuels, and get the liquid and gaseous products which is extracted from briquette pyrolysis, This achieves the efficient multi-level use of resources[3]. Although there is a research foundation on pyrolysis characteristics of lignite, the pyrolysis characteristics of the products of the binderless hot-briquetted lignite still has not been reported yet. In this paper, pyrolysis characteristics of the binderless hot-briquetted lignite were studied taking Bori lignite as raw materials to provide some basic data for developing effective lignite processing ways.

2. Experimental

2.1. Sample preparation

Lignite:

An elderly lignite, from Borixile east of Inner Mongolia, was taken as raw materials, and was reduced sub-sampling according to national standard[6]. The coal sample was placed in the air to reach moisture equilibrium as reserve.

Lignite briqutte:

The air-dried lignite was broken and sifted. The coal simple which's particle size <3mm, was dried by quick airflow and molded at 300℃ in 20min. under a pressure of 200KN [7]. Then the binderless hot-briquetted with a dimension of 20×30×5mm was produced.

The index of lignite and its binderless hot-briquetted lignite was given in Table 1.

Table 1 Proximate and ultimate analyses of coal and briquetle

Index	M_{ad}/%	A_d/%	V_d/%	FC_d/%	C_d/%	H_d/%	N_d/%	O_d/%	$S_{t,d}$/%
Lignite	23.53	9.79	44.19	46.02	58.77	3.95	0.71	17.6	0.27
Briquette	*7.83*	*9.34*	*39.54*	51.12	64.12	4.31	0.78	19.21	0.29

2.2. Pyrolysis

The coal samples were tested in a fixed bed reactor under pyrolysis conditions. The pyrolysis was carried out with 600g of samples by a stainless steel reactor (1000(length)×100mm(i.d)). The reactor was heated at a rate of 10~15℃/min up to the final temperature by an electric furnace thermally. 90min. was taken as a representative residence time, and stop heating after reaching the residence time. Weigh the material when the experimental apparatus cooling to room temperature, and analysis of the relevant properties of semi-coke.

2.3. Separation of tar, gas and water

The gaseous products produced in the pyrolysis process was coolde to room temperature through multi-level indrect cooling method, and the liquid tar and water mixture was collected and separated. The cooled gas flow through the gas meter and gas flow was recorded, gas samples were collected at any time with airbags to be analysed by gas chromatography(GC).

The mixture of tar and water was placed into distillation apparatus and was distilled. The mixture of light oil and water was produced and further separated using a separated funnel. Finally, the heavy tar, light oil and water was obtained respectively.

2.4. Analysis instrument

SEM: JSM7401 ultra-high resolution field emission scanning electron microscope, Japan;
GC: SP-2100A type, Beijing Temple's North Division;
KJ-7071-type fall test machine.

3. Results and discussions

3.1. Properties of the semi-coke

The briquette semi-coke that had a 90min. holding time was taken as the representative sample for industrial and elemental analysis, and the results were shown in Table 2.

With the pyrolysis temperature increasing, the moisture and the volatile content of the semi-coke decreased,. And the fixed-carbon content increased. When the pyrolysis temperature increased from 450℃ to 900℃, the moisture content in semi-coke decreased from 2.27% to 1.01%, the dry basis volatile decreased from 20.77% to 1.25%, and the dry basis fixed-carbon increased from 59.69% to 73.56% as shown in Table 2, It was because of the decreasing of moisture and volatile that the ash content in semi-coke relatively increased. The dry basis ash content of semi-coke was 20%-25%. Visibly, the variation of the industrial analysis of briquette semi-coke was similar to the products of lignite[6,7]. In the pyrolysis temperature range of 450-650℃, the yield of semi-coke decreased sharply from 77% to 65%. When the pyrolysis temperature increased above 700℃, the decreasing rate of the semi-coke yield slowed, indicating that most of the volatiles have been released; and when the temperature increase above 800℃, the semi-coke yield unchanged almost.

Table 2 Proximate, yield and mechanical strength analysis of briquette semi-coke（holding time 90min.）

Temperature/℃	M_{ad} /%	V_d /%	A_d /%	FC_d /%	Yield/%	Falling strength/%	Compressive strength/N
450	2.27	20.77	19.55	59.69	76.45	45.31	145.22
550	1.97	13.08	21.61	65.31		45.69	146.21
600	2.03	7.06	22.92	70.02		47.79	149.77
650	1.65	6.77	23.29	69.94	65.04	53.03	151.29
700	1.55	4.38	23.74	71.89		60.88	157.24
750	1.52	2.67	24.21	73.12	63.45	62.83	158.01
800	1.91	2.16	23.42	74.42	63.18	63.21	158.39
850	1.27	1.87	24.90	73.23	62.88	65.69	160.27
900	1.01	1.25	25.18	73.56		66.87	165.60

However, the lignite briquette semi-coke not only had a low volatile content and high fixed-carbon content, but also had a high mechanical strength. In Table 2, with the pyrolysis temperature increasing, both falling strength and compressive strength of the semi-coke were increased. When the pyrolysis temperature reaches 700℃, the strength of semi-coke increased clearly, and the falling strength and compressive strength reached 60.88% and 157.24N respectively, significantly higher than the normal semi-coke of lignite [8,9]. Obviously, the briquette semi-coke was more suitable for carbon reducing agent or high quality raw materials of fixed-bed gasification.

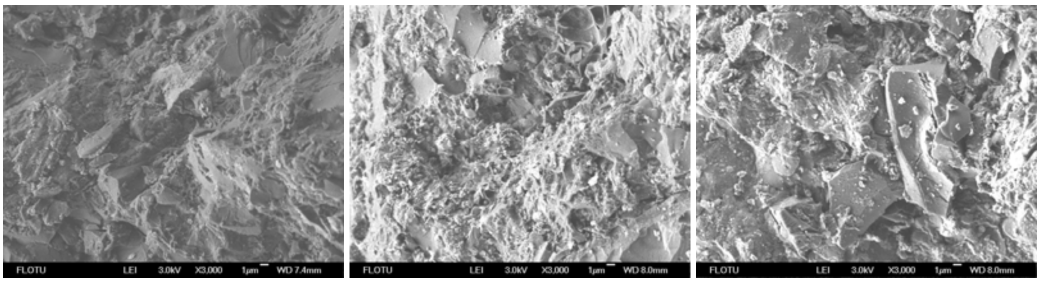
The temperature also had a significant effect on the element content of briquette semi-coke. It can be seen from Table 3, with the increasing of pyrolysis temperature, the hydrogen content decreased gradually, the carbon content gradually increased, and the H /C decreased. Oxygen content changed significantly in semi- coke: When the pyrolysis temperature increased from 450℃ to 550℃, the oxygen content decreased from 5.63% to 0.38%; and when the pyrolysis temperature reached 650℃, the oxygen in the semi-coke disappeared entirely. The sulfur content in the briquette semi-coke increased slightly, and the nitrogen content didn't change significantly.

Table 3 Elements analysis of briquette semi-coke（holding time 90min.）

Temperature/℃	C_d/%	H_d /%	O_d%	N_d/%	S_t /%	H/C
450	70.27	2.67	5.63	0.84	0.30	0.038
550	73.76	2.07	0.38	0.9	0.32	0.028
650	77.34	1.9	0	0.88	0.38	0.025
750	79.05	1.17	0	0.58	0.39	0.015
800	79.98	0.84	0	0.45	0.39	0.010
850	79.95	0.7	0	0.37	0.41	0.009
900	80.9	0.49	0	0.32	0.44	0.006

3.2. SEM of semi-coke

The micro morphology of the briquette semi-coke produced at typical pyrolysis temperature under 3000 times magnification was shown in Fig. 1. At 400℃, it was due to the release of volatile, the pore structure formed in the semi-coke, and clear honeycomb-like pore structure distribution was shown in the local; at 600℃, the release of volatile increased, a larger size pore structure distribution appeared, while the small pore became the large pore, the cracks of large pore appeared; at 800℃， the large apparent melt pore appeared, the clear soft surface and the collapsed cracks structure formed.



(a)400℃ (b)600℃ (c) 800℃

Figure. 1 SEM photos of briquette semi-coke prepared at different temperature

3.3. Properties of the liquid

The hot gases produced in the pyrolysis process became a mixture of tar and water through cooling unit, and the heavy tar, light oil and water was obtained respectively after the mixture distillation and the separation of the tar and water. The variation of the tar and water yield under different pyrolysis temperature was given in Table 4.

As can be seen from Table 4, in the pyrolysis temperature range between 400℃ and 500℃, the water yield in the liquid product increased significantly from 12.45% to 17.61%, 5.16% increased; in the temperature range between 500℃ and 900℃, the water yield only increased from 17.61% to 18.37%, 0.76% increased. It indicated that in the range between 400℃ and 500℃, the water was produced not only from the release of raw material but also from the pyrolysis water.

When the temperature was 550℃, there was a maximum tar yield of 3.39%. With the temperature increasing further, the tar yield began to decrease. In the temperature range between 400℃ and 600℃, there was a high content(1.25%-1.3%) of light oil in the tar. At the temperature between 650℃ and 800℃, the content of light in the tar decreased relatively. When the temperature exceeded 850℃, the light oil content was less than 1%. It showed that with the temperature increasing, the pyrolysis products may occur further Polycondensation reaction or Carbonation reaction[10], which caused the decrease of small molecules oil yield. The variation of heavy oil is similar to the tar at different pyrolysis temperature, and the variation was not obvious.

Table 4 Tar and water yield in different pyrolysis temperature（holding time 90min.）

Temperture/℃	Tar-water（%）	tar（%）	Light oil（%）	Heavy tar（%）	Water（%）
400℃	15.22	2.77	1.25	1.52	12.45
500℃	20.46	2.85	1.27	1.58	17.61
550℃	19.74	3.39	1.6	1.79	16.35
600℃	20.43	3.08	1.3	1.78	17.35
650℃	20.93	2.80	1.07	1.73	18.13
700℃	21.37	2.75	1.06	1.69	18.62
750℃	22.08	2.73	1.05	1.68	19.35
800℃	21.88	2.71	1.03	1.68	19.17
850℃	20.82	2.44	0.97	1.47	18.38
900℃	20.75	2.38	0.9	1.48	18.37

3.4. Releasing characteristic of each pyrolysis gas component

With the pyrolysis temperature increasing, the pyrolysis gas yield changed remarkably. As the Table 5 showed, in the temperature range between 400℃ and 650℃, the yield of pyrolysis gas increased significantly from 4.45% to 22.13%, 17.68% increased. With the temperature increasing further, the increase rate of gas yield decreased. When the temperature increased from 700℃ to 800℃, the gas yield increased from 22.36% to 22.90%, only 0.54% increased. When the pyrolysis temperature was above 800℃, the volatile of briquette had released completely, and the gas yield reached the maximum.

Table 5 Effects of pyrolysis temperature on gas yield （holding time 90min.）

Temperature/ ℃	*400*	*450*	*550*	*600*	*650*	*700*	*750*	*800*	*900*
Yield/%	4.45	8.27	17.17	18.6	22.13	22.36	22.76	22.9	22.9

The variation of the releasing rate of each pyrolysis gas component with the temperature increasing was obtained through tracking and analyzing the content of each pyrolysis gas under different pyrolysis conditions by GC. The variation of each component of gas releasing rate at different pyrolysis temperature was given in Fig. 2(a), (b), (c) separately.

(1) Variation of hydrocarbon(C_1~C_4)

In the process of pyrolysis, the releasing of CH_4 was due to the fracture of fat chains that contained methyl functional group and side chains of aromatic[9]. As fig. 2(a) showed, the distribution range of CH_4 curve is very wide. The CH_4 started releasing at 400℃; With the temperature increasing, the amount of CH_4 increased rapidly, and had a maximum (0.80L/min.) at 750℃, but decreased slightly later.

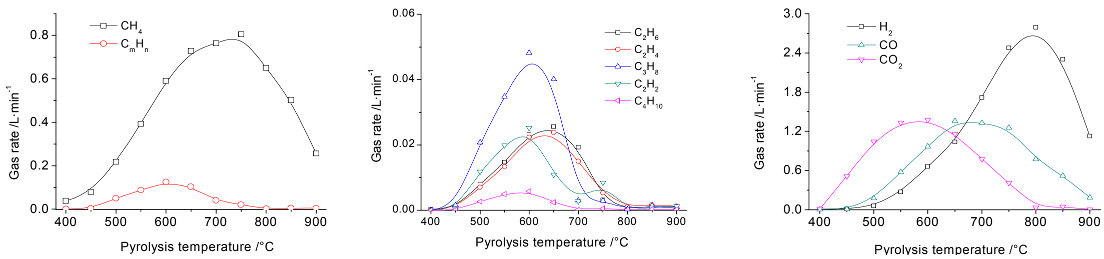
The Fig. 2(b) showed that: When the temperature increased above 450℃, the releasing amount of C_2~C_4 hydrocarbon gas increased, and had a maximum. And the releasing amount of C_2H_2, C_3H_8 and C_4H_{10} reached the maximum at 600℃, with being 0.025 L/min.、0.048 L/min. and 0.0058 L/min. respectively. The releasing amount of C_2H_4 and C_2H_6 had a maximum (0.024 L/min., 0.026 L/min.) at 650℃.

It was also showed in Fig. 2(a) that: The total content of C_mH_n was low in the pyrolysis gas, compared with CH_4. The gas released mainly in the temperature range of 450~750℃, and almost no these hydrocarbon gas was produced after 750℃; However, there's still a considerable releasing amount of CH_4 (0.26 L/min.), when the pyrolysis temperature reached 900℃.

(2) Variation of H_2, CO and CO_2

The Fig. 2(c) showed that, H_2 was produced slowly from 400℃. The yield of H_2 increased rapidly after 500℃, and reached the maximum (2.79 L/min.) at 800℃. With the pyrolysis temperature increasing continually, the H_2 yield start decreasing, and the releasing amount was 1.12 L/min. at 900℃. Visibly, the releasing temperature range of H_2 was wide, but a large number of H_2 released focusing on the temperature range between 700℃ and 850℃.

In the pyrolysis process, CO and CO_2 was mainly produced from variety of oxygen functional groups in the coal. The forming of CO_2 was mainly due to the removal of carboxyl, partly due to the fracture and decomposition of oxygen heterocyclic, such as O—C=O. As the Fig. 6(c) showed, CO_2 released earlier than CO, and the releasing amount of CO_2 reached a maximum (1.37 L/min.) between 550℃ and 600℃, the releasing rate decreased after 600℃. The releasing amount of CO had a maximum (1.35 L/min.) between 650℃ and 750℃, and the releasing rate decreased after 750℃.



(a)CH_4, C_mH_n (b) C_2H_6, C_2H_4, C_2H_8, C_2H_2, C_4H_{10} (c) H_2, CO, CO_2

Fig.2 Effects of pyrolysis temperature on gas releasing rate

4. Conclusion

(1) With the pyrolysis temperature increasing, the yield of hot-briquetted lignite semi-coke decreased, the H/C of semi-coke decreased significantly, the O element reduced quickly, and disappeared when the temperature was 650 ℃. The strength of semi-coke increased obviously, the falling strength and compressive strength reached 60.88% and 157.24N respectively. The low temperature semi-coke appearance seemed like honeycomb. With the temperature increasing, the number of large pore increased and softening surface and collapsed cracks appeared.

(2) At the temperature range between 400℃ and 900℃, the change range of water yield in the pyrolysis liquid product was between 12.25% and 19.35%. The total yield of tar was 2.77~3.39%, among which, the yield of heavy was 1.52~1.79%, and the light tar yield was 1.25~1.6%.

(3) At the pyrolysis temperature between 400℃ and 800℃, the gas yield increased rapidly from 4.45% to 22.90%. And the releasing amount of CH_4 reached the maximum(0.80L/min.) at 750℃; the releasing amount of C_2H_2, C_3H_8 and C_4H_{10} had a maximum at 600℃, being 0.025 L/min., 0.048 L/min. and 0.0058 L/min. respectively; the releasing amount of C_2H_4 and C_2H_6 reached the maximum at 650℃, being 0.024 L/min. and 0.026 L/min. respectively. The releasing of H_2, CO_2 and CO reached the maximum at 800℃.550~600℃,650~750℃respectively, with their values being 2.79L/min,1.37 L/min and1.35L/min respectively.

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